

## **Study of Natural Analogues for the Comprehension of Gas Migration Mechanisms**

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### **Introduction**

Soil gas anomalies are useful to recognize influences of surface features on natural gas migration. The study of the association of different gases (with different origin and physical/chemical behavior), the collection of a large number of samples during periods of stable meteorological and soil moisture conditions (e.g., during dry season) and the use of appropriate statistical treatment of data are fundamental in the comprehension of gas migration mechanism.

Gas geochemistry has been proven to be a reliable and simple technique to apply, at different scales, to many geological scenarios [Quattrocchi et al. 2001; Baubron et al. 2002; De Gregorio et al. 2002; Pizzino et al. 2002; Lewicki et al. 2003; Voltattorni et al. 2009; Lombardi and Voltattorni, 2010]. The study of spatial distribution of soil gas anomalies, at the surface, can give important and interesting information on the origin and processes involving deep and superficial gas species. This information can be applied and studied in different frameworks, for example:

1. geological sequestration of anthropogenic CO<sub>2</sub> to reduce the amount of greenhouse gases released to the atmosphere. Natural gas emissions represent extremely attractive surrogates for the study and prediction of the possible consequences of leakage from geological sequestration sites of anthropogenic CO<sub>2</sub> (i.e., the return to surface potentially causing localized environmental problems).
2. radionuclide migration in the study of high-level radioactive-waste isolation systems. The main approach is to study the natural migration of radiogenic particles or elements throughout clay formations that are considered an excellent isolation and sealing material due to their ability to immobilize water and other substance over geological timescales.

### **Sampling and analytical procedures**

Soil gas surveys can be performed at both regional (e.g., sampling grid: 1 sample/km<sup>2</sup>) and local scale (detailed sampling grid including profiles and/or transects) on the basis of the research goal. The surveys should be performed during summer or dry periods to avoid climatic factors which may affect soil gas values [Hinkle, 1994].

Shallow soil gas samples are obtained using a 1 m stainless steel probe fitted with a brass valve: this system enables soil gas to be collected and stored in metallic containers (with a vacuum 10<sup>-2</sup> atm) for laboratory analysis or to be pumped for on-site Rn analysis. Radon determination is accomplished in the field with an EDA Instrument RDA-200 Radon Detector.

Generally, the studied gases include major (N<sub>2</sub>, O<sub>2</sub>, CO<sub>2</sub>) and trace (<sup>4</sup>He, H<sub>2</sub>) gases and light hydrocarbons (C<sub>1</sub> to C<sub>4</sub>) that are analysed using a Fison Instrument GC-8000 Series gas-chromatograph.

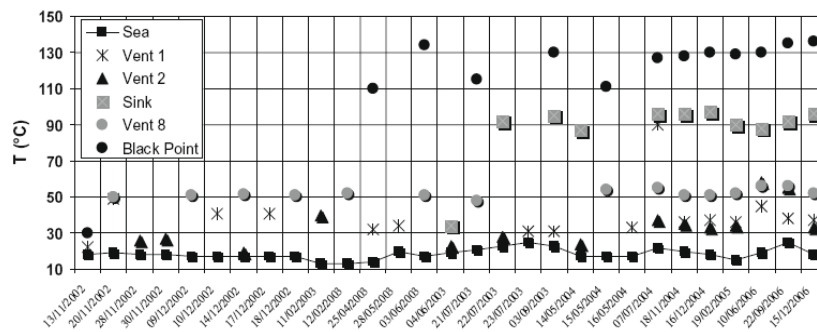
A specific technique has been developed to collect submarine samples [Caramanna et al. 2005] in proximity of gas vents. In order to collect free/dry gas samples, a plastic funnel is inverted (30 cm diameter with 12 kg ballast around the lower ring) and placed precisely on the gas vent to be sampled. The funnel is connected, through a silicon hose, to a Pyrex glass flask with twin valves. This flask is pre-filled with air at a pressure above that of the hydrostatic pressure expected at the sampling depth in order to stop seawater from entering the sampler.

### **Results: study of natural gas emissions**

An area in proximity of Panarea Island (Aeolian Islands, southern Italy) was interested by a huge submarine volcanic-hydrothermal gas burst during November, 2002. The submarine gas emissions

chemically modified seawater causing a strong modification of the marine ecosystem causing the death of mainly benthonic life forms and serious damage to the sea-grass *Posidonia oceanica* [Voltattorni et al. 2009].

Gases have been collected from the seafloor at variable depths (depending on gas emission point depth). The temperatures of leaking fluids are variable at the different gas emission points (Figure 1): highest temperature measurements refer to Black point ranging between 110 °C and 137 °C, excepting the first measurement. Lower temperatures (mean value: 86.7 °C) have been measured at the Sink point and at Vent 8 (mean value: 52.11 °C). According to Capaccioni et al. [2007], a possible explanation for the temperature variability at the different gas emission points is related to an inferred magmatic system centred on or closer to Black point and whose diameter probably does not exceed a few hundred meters.



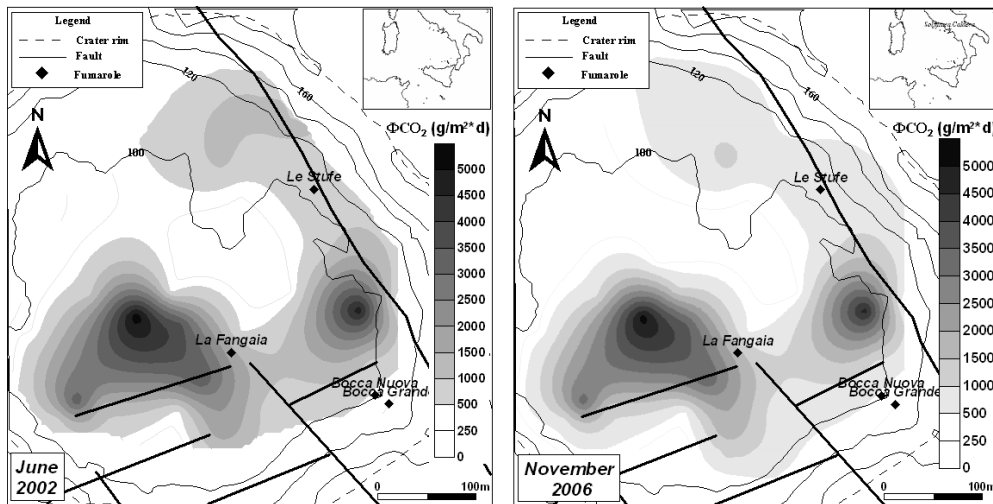
**Figure 1.** Temperature measurements at Panarea vents. Fluids from vents are very hot (especially from Sink and Black point with temperatures >90 °C) but due to their low flow, they do not affect temperatures of the surrounding seawater.

All of the collected gases are CO<sub>2</sub>-dominant (the content varies from a minimum of 83.64 vol. % to a maximum of 98.43 vol. %). The CO<sub>2</sub> leakage varies at the different vents being higher at the Black point and lowest at the Sink point. However, median values are very similar for each vent suggesting a common degassing input linked to local tectonic features. In fact, all the gas emission points are located along N–S, E–W and NE–SW oriented active faults controlling the Aeolian Volcanic District.

Another natural degassing area is the Phlegraean Fields magmatic system that is still active, as the last eruption occurred in 1538 A.D. at Monte Nuovo. Faults affecting the Phlegraean Fields caldera follow two preferred strikes, NW–SE and NE–SW, that also affect the Campanian Plain and the inner sectors of the Apennine belt [Orsi et al. 1996].

The Phlegraean Fields Caldera has been investigated, during November 2006, by means of a detailed soil-gas survey in the inter crater sector, during which 54 soil gas flux measurements (1 sample/50–100 m) have been performed through the method of the accumulation chamber.

The  $\Phi_{\text{CO}_2}$  values range from 0 to 5500 gr/m<sup>2</sup>\*d with an average of 1127.32 gr/m<sup>2</sup>\*d. The highest flux values were found in the “La Fangaia” and near the “Bocca Grande” and “Bocca Nuova” fumaroles. The same area was investigated during June 2002 [Voltattorni et al. 2006] and a comparison of the two surveys (Figure 2) performed in different years and seasons, has highlighted that the highest  $\Phi_{\text{CO}_2}$  values are always within an area bordered by faults and fractures, confirming that the degassing process is strictly related to local tectonic structures.

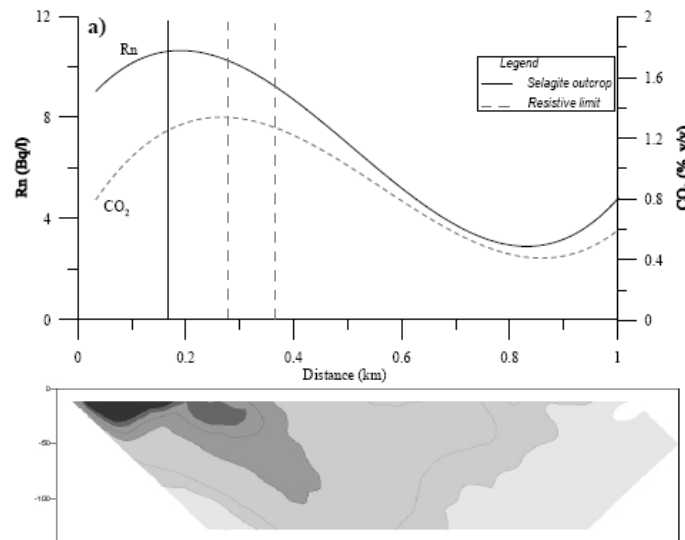


**Figure 2.** Contour maps of CO<sub>2</sub> fluxes at Phlegraean Fields Caldera. The results from two surveys performed in different years (June 2002 at the left and November 2006 at the right) and seasons highlights that the highest  $\Phi_{CO_2}$  values are always within an area bordered by faults and fractures.

### Results: study of natural radionuclide migration

The physical properties of thermally altered clays of the Orciatice area (Tuscany, Central Italy) were studied as they could act as geological barriers to radionuclide migration in high-level radioactive-waste isolation systems. The study was performed through detailed soil gas surveys in order to define the gas permeability of the clay unit [Voltattorni et al. 2010].

A total of 1086 soil gas samples was collected in the Orciatice area. Highest soil gas values ( $^{222}\text{Rn} > 25$  Bq/L,  $\text{CO}_2 > 2\%$ , v/v) occur in the south-western part of the studied area (characterized by the presence of the igneous body outcrop named Selagite) and along a narrow belt, with direction NNW-SSE, where metamorphosed clays (named Termantite) are present. All over the north-eastern sector, in non metamorphosed clays, radon and carbon dioxide values are very similar to background values reported in literature ( $\text{Rn}$ : 10-15 Bq/L,  $\text{CO}_2$ : 0.5 %,v/v). As radon and carbon dioxide values seem to decrease gradually from Selagite outcrop towards un-metamorphosed clays, soil gas data set were projected along one longitudinal lines coinciding with a performed geoelectrical profile. Figure 3 shows polynomial regression (3<sup>rd</sup> degree) of radon and carbon dioxide values plotted against the distance from a reference point. The overlapping peaks in the radon-carbon dioxide plots should confirm that the soil gas distribution is linked to clay alteration degree. In fact, highest CO<sub>2</sub> and Rn values were found between Selagite outcrop and the first resistive limit, in a narrow belt characterized by a high alteration degree and, probably, by an intense shallow fracturing. On the other hand, after the second resistive limit, where clays did not undergo the effects of the intrusive body, radon and carbon dioxide values are in agreement with the mean values reported in literature excepting in the last 200m of the profile where values slightly increase again.



**Figure 3.** Comparison between polynomial regression (3° degree) map and geoelectrical profile. Rn and CO<sub>2</sub> graphs highlight slightly decreasing trends of soil gas values towards the NE, from Selagite outcrop until un-metamorphosed clays.

## Conclusions

On the basis of the many achieved results, it can be said that soil gas prospection constitutes a powerful tool to identify complex phenomena occurring within the crust. The comprehensive approach followed in this study has provided insights on the spatial influence of tectonic discontinuities and geology on gas migration toward the surface. Soil gas measurements, performed at different scales, involved gaseous species with very different geochemical behaviour. Soil gas surveys yielded different features of the anomalies, reflecting the different gas bearing properties of the pathways along which gases can migrate.

As soil gas distribution can be affected by some phenomena related to the climatic factors, soil moisture and gas behaviour (mobility, solubility, and reactivity), a multivariate study including a large number of gaseous species has been considered.

However, independent from gas origin, all the results show that gases migrate preferentially through zones of brittle deformation and enhanced permeability. In order to quantify, the spatial influence of fault geometry and geochemical properties on the distribution of soil gases, the geostatistical approach (i.e., variograms) is necessary.

Because of the very high variability of gas concentrations at the surface, soil gas prospection appears necessary in order to select potential optimum sites for surveillance to identify, for example, regional changes of strain fields or variations in toxic emanation. Due to the complex relationship between geology and local phenomena, a network of geochemical stations would be much more useful.

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